

# COMPACT FUEL CELL POWER SUPPLIES WITH SAFE FUEL STORAGE

M. R. Powell\*

MesoSystems Technology, Inc.  
Kennewick, Washington 99336

A. S. Chellappa and T. R. Vencill

Intelligent Energy, Inc.  
Albuquerque, New Mexico 87107

## ABSTRACT

A compact, lightweight hydrogen-production system was developed for fuel-cell-based power supplies. Anhydrous ammonia is decomposed thermocatalytically in a microreactor to produce a fuel-cell feed gas. For an electrical energy capacity of 1250 W-h, this system has an energy density of 500 W-h/kg, which is roughly twice that of state-of-the-art batteries. Despite its energy-density advantage, this ammonia-based power supply will not likely be deployed in military or commercial markets unless safety concerns related to the possible rapid release of ammonia are resolved.

Semi-permeable, high-void-fraction materials were developed to address the issue of ammonia safety. Liquefied ammonia is loaded into a monolithic block of safe-storage material, which is installed in a suitable lightweight tank. In the event of tank puncture or leakage from another system component, the release of toxic/flammable gas to the surroundings is restricted by the safe-storage material. Gas release from the safe-storage material is on the order of 1 g/min, which is sufficiently slow to avoid rapid formation of dangerous ammonia concentrations in an enclosed space. These safe-storage materials can also be used for storage of liquefied hydrocarbons such as propane and butane.

## 1. BACKGROUND

Improvements in the design and manufacture of hydrogen/air fuel cells have increased interest in use of fuel cells as a replacement for batteries and other, larger power supplies (e.g., vehicle engines). Because they can operate on very energy-dense fuels, and they are quiet and efficient, fuel-cell-based power supplies are considered promising competitors to lightweight batteries.

The most promising fuel cells operate using hydrogen gas for fuel and oxygen (from air) as an oxidant. Unfortunately, reliable, convenient, and compact hydrogen sources do not yet exist, so fuel cells have yet to receive

widespread commercial or military use. The fuel cells, however, represent relatively mature technology and are commercially available.

Several approaches are available for hydrogen generation and/or storage. These include hydrocarbon and methanol fuel reforming, hydrogen absorption into metal hydrides, hydrogen-generating chemical reactions, and ammonia decomposition (Blomen and Mugerwa, 1993; Bloomfield et al., 1995).

Our work focuses on hydrogen-generation approaches employing liquefied gas fuels such as propane, butane, and ammonia. While these fuels have the advantage of simplified reactor and fuel-delivery systems, pressurized fuel presents safety concerns related to the flammability of propane/butane and the toxicity of ammonia.

Under a Phase II Small Business Innovation Research (SBIR) contract with the U.S. Army Research Office, MesoSystems and Intelligent Energy are developing an intrinsically safe fuel-storage system. We are focused primarily on storage of anhydrous ammonia to support ammonia-based hydrogen generators developed previously by us (Powell et al., 2001; 2002) and others (e.g., Schmidt et al., 2002). Some of our efforts, however, are directed at safe storage of butane and propane, which are liquefied gas fuels suitable for use in other types of hydrogen generators.

This paper describes two related technological advancements: (1) a lightweight, ammonia-based hydrogen generator; and (2) lightweight, intrinsically safe ammonia storage tanks. Because more detailed descriptions of the hydrogen generator are available in other publications (Powell et al., 2001; 2002) greater attention is paid to our more recent and heretofore unpublished work on safe storage of toxic and flammable liquefied gases.

## 2. AMMONIA-BASED HYDROGEN GENERATOR

Ammonia decomposition and ammonia-based chemical reactions are attractive methods for hydrogen generation

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>00 DEC 2004</b>		2. REPORT TYPE <b>N/A</b>		3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Compact Fuel Cell Power Supplies With Safe Fuel Storage</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Meso Systems Technology, Inc. Kennewick, Washington 99336; Intelligent Energy, Inc. Albuquerque, New Mexico 87107</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>See also ADM001736, Proceedings for the Army Science Conference (24th) Held on 29 November - 2 December 2005 in Orlando, Florida. , The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>8</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

because the required chemical reactors tend to be relatively small, simple, and easy to control. This section discusses some of the advantages and disadvantages of ammonia as a fuel for compact-power systems and provides a description of the ammonia-based hydrogen generator developed by the authors.

## 2.1 Extracting Hydrogen from Ammonia

Ammonia is produced industrially from natural gas and nitrogen via the Haber-Bosch process in which methane is reformed to make hydrogen, which is reacted with nitrogen in the presence of a catalyst under high pressure (Twigg, 1997). Hydrogen can be thermocatalytically extracted from ammonia simply by reversing the ammonia-synthesis reaction. In the presence of a catalyst and at temperatures typically in excess of 500°C, ammonia decomposes to form hydrogen and nitrogen via the reaction:



Production of ammonia by thermocatalytic decomposition is the method used for the hydrogen-generation system described in this paper.

Hydrogen can also be extracted from ammonia by reacting ammonia with  $\text{LiAlH}_4$  (Schmidt et al., 2002). This approach provides hydrogen production with minimal startup time, but both the  $\text{LiAlH}_4$  and the ammonia must be replaced with every use.

## 2.2 Why Hydrogen from Ammonia?

Ammonia decomposition for fuel-cell applications has received less attention than hydrocarbon-based approaches because of ammonia's toxicity and foul odor, and because it is not economical for power production except in remote, low-power applications (Appleby and Foulkes, 1989; T-Raissi, 2002). In spite of these drawbacks, ammonia is an attractive hydrogen source for at least two reasons: (1) The usable hydrogen per kilogram of fuel is relatively high; and (2) Ammonia-based hydrogen generators are simpler and likely can be deployed sooner than hydrocarbon-based fuel reformers.

Ammonia has a lower heating value of about 6000 W-h/kg. Roughly 14% of this energy is required to supply the endothermic ammonia-decomposition reaction, so the effective *hydrogen* energy available from ammonia is about 5100 W-h/kg. Assuming a maximum fuel-cell efficiency of about 50%, the resulting maximum energy density of an ammonia-based, fuel-cell power system is about 2600 W-h/kg. This value compares well with the energy density of other fuels such as methanol, methane, and gasoline as shown in Fig. 1. Extraction of hydrogen from the hydrocarbon fuels is usually performed via steam

reforming, which requires addition of water to the reaction chamber. Including the required water mass reduces the effective energy density of these fuels to between 2000 and 4000 W-h/kg.

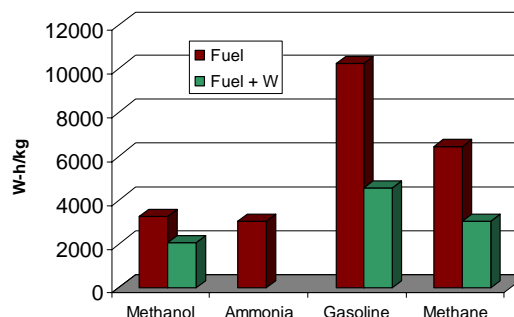


Fig. 1. Hydrogen energy densities for various fuels

The fuel energy densities shown in Fig. 1 compare favorably with those of battery-based power supplies. State-of-the-art batteries (e.g., Zn/air batteries and the  $\text{LiMnO}_2$  Primary/15 Pouch used by the U.S. Military) have an energy density of up to 300 W-h/kg. This energy density is roughly a factor of ten lower than the energy densities for the fuels included in Fig. 1. However, the values in Fig. 1 do not include the mass of the fuel cell and other components required to convert the fuels to hydrogen. To take advantage of the high energy densities of fuels such as methanol, ammonia, and gasoline, the mass of the fuel cell, hydrogen generation system, and fuel-storage tank must be minimized.

## 2.3 Simple, Compact Microreactor

Reduction of hydrogen-generation system mass is a key motivation for pursuit of ammonia as a hydrogen source for fuel cells. Conversion of ammonia to hydrogen is a relatively simple, single-step process. Conversion of hydrocarbon-based fuels, however, often requires multiple chemical reactors: one to convert the hydrocarbon to synthesis gas ( $\text{H}_2$  and  $\text{CO}$ ), another to convert most of the  $\text{CO}$  to  $\text{CO}_2$ , and yet another reactor to further reduce the  $\text{CO}$  concentration to levels the fuel cell can tolerate. By contrast, ammonia decomposition can be accomplished in a single chemical reactor. This fact allows for a significant reduction in the size, mass, and complexity of the hydrogen-generation system when ammonia is used as the fuel source.

Over the past decade, there has been increasing interest in the use of microreactors for chemical processing. The small size and low mass of these reactors make them well suited for portable applications. The chemical processing rates of microreactors are higher than would be expected based solely on a linear extrapolation of large-scale reactor performance. With proper design, heat- and mass-transfer rates in microreactors can be orders of magnitude higher

than those typically obtained in industrial-scale reactors. Thus, in a microreactor, it is often possible to operate at short reactor residence times – close to the residence time required by the intrinsic reaction kinetics. The microreactor used in our 50-watt, ammonia-based hydrogen generator is shown in Fig. 2.



**Fig. 2.** MesoChannel™ ammonia-decomposition reactor

Small reactor size and low mass provide several advantages. The low mass helps to maintain portability of the device and reduce the time required for heating the reactor to its operating temperature. Small size reduces the amount of insulation required to keep heat loss to ambient at acceptable levels.

## 2.4 Prototype System

The MesoChannel™ reactor shown in Fig. 2 was integrated with the required flow-control components, temperature-control electronics, recuperative heat exchangers, an adsorbent column, aerogel-based insulation, and a 0.8-liter ammonia storage tank. Fig. 3 shows the integrated components. The system mass is 1570 grams including the ammonia. The 0.8-liter ammonia storage tank will hold up to 420 grams of anhydrous ammonia, which will yield 1250 W-h of electrical energy from a fuel cell (assuming 17 W-h per gram of hydrogen). Including the mass of the ammonia, this prototype produces hydrogen with an apparent energy density of 800 W-h/kg. When integrated with a 1-kg fuel cell, the resulting power supply has an energy density of 500 W-h/kg, which is roughly twice that of state-of-the-art batteries. Increasing the capacity of the ammonia-storage tank improves the overall energy density considerably provided a lightweight storage tank is used. Energy densities in excess of 1500 W-h/kg can readily be attained when ammonia tanks larger than 2-kg capacity are employed.

The ammonia-based power supply is easily recharged by refilling the storage tank with ammonia. Ammonia is a widely produced industrial chemical that is available at low cost. Enough ammonia for 1000 W-h of energy can be purchased at current prices for less than \$1. This compares favorably with the high cost of the Primary/15 Pouch batteries, which are roughly \$700 per 1000 W-h of energy. Provided the cost of the fuel cell and fuel reformer can be kept reasonable, ammonia-based power generation offers considerable cost savings in addition to a reduction in power-supply mass.



**Fig. 3.** Ammonia-based hydrogen generator

Despite the promise of lightweight, low-cost power supplies based on anhydrous ammonia, commercial and military interest is severely limited by concerns over ammonia's toxicity. Our efforts toward solving this problem are described in the next section.

## 3. SAFE AMMONIA STORAGE

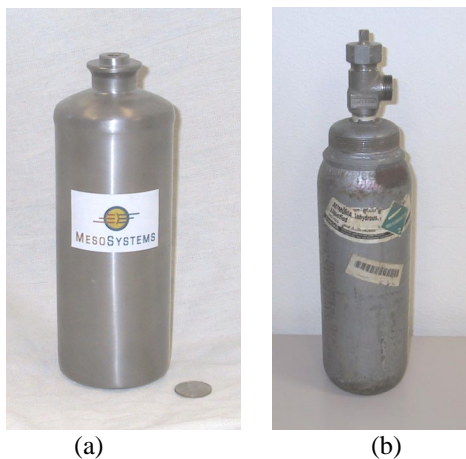
Before ammonia-based hydrogen generators will gain acceptance, the problem of safe ammonia storage must be addressed. Ammonia is a toxic gas that can rapidly damage the eyes and respiratory tract upon exposure to concentrations in the range of 500 to 1000 ppm. Even brief exposure to higher concentrations (>5000 ppm) can lead to respiratory failure and death (Nielsen, 1995). An ammonia-based hydrogen generator operating in an enclosed environment must not have the potential for rapid ammonia release as this may be harmful or even deadly for surrounding personnel.

### 3.1 Drawbacks of Conventional Storage Tanks

The ammonia-based hydrogen generators currently under development (e.g., Powell et al., 2002; Schmidt et al., 2002) employ lightweight storage tanks made from either aluminum or titanium (see Fig. 4a). These tanks have a mass of approximately 120 g and an ammonia storage volume of 0.8 liters. The lightweight storage tanks (aluminum and titanium) are designed to withstand over 1000 psig to ensure they do not burst in response to ammonia vapor pressure, which can exceed 250 psi at credible ambient temperatures. However, these storage tanks are not designed to withstand bullets or puncture from sharp objects.

Department of Transportation (DOT) approved ammonia storage tanks employ thick metal walls and are generally much heavier. Fig. 4b shows a DOT-approved

tank with an ammonia capacity of 1.5 liters and an empty mass of 2.3 kg. When properly handled, the DOT-approved tank provides an acceptable level of protection from accidental ammonia release because rupture or puncture of the tank is unlikely.



**Fig. 4.** (a) 0.8-L titanium tank; (b) 1.5-L DOT tank

As discussed earlier, anhydrous ammonia has a fuel-cell energy density of 2600 W-h/kg. If ammonia is stored in a 0.8-liter titanium tank, the effective energy density (including only the mass of ammonia and the tank) is reduced to 2000 W-h/kg. Use of the 1.5-liter, DOT-approved tank yields an effective energy density of 750 W-h/kg.

Thus, there are two competing characteristics to consider in the design of an ammonia-storage tank: safety and effective energy density. Reductions in tank wall thickness improve the effective fuel energy density, but at the cost of reduced safety.

Tank puncture/rupture is only one failure mode that can result in an unsafe release of ammonia to the surroundings. Failure of tubing and/or reactor components downstream of the ammonia-storage tank can result in rapid release of ammonia. Before ammonia-based hydrogen sources can be widely marketed, the ammonia storage tanks must be improved to guard against rapid ammonia release in the event of tank puncture *and* failure of any downstream components. Conventional ammonia storage tanks cannot simultaneously meet the requirements for safety and high effective energy density. A better approach is needed.

### 3.2 Desired Properties of a Safe-Storage System

A safe means of storing anhydrous ammonia must be developed before ammonia-based hydrogen supplies for fuel-cell power systems will gain acceptance by commercial and most military customers. To meet this need, the ammonia-storage system must have the following characteristics:

**High storage density:** One of the principal benefits of using ammonia as a hydrogen source is the fact that ammonia is nearly 18%wt. hydrogen. If the ammonia storage system adds significant mass to the mass of stored ammonia, then ammonia becomes less attractive as a hydrogen source. The target hydrogen-storage density<sup>1</sup> is 2.0 kWh/kg, which implies ammonia comprises at least 75% of the total mass; the tank and any other storage-related components comprise the remaining 25%.

**Low overall volume:** Portable power systems become less useful as their volume increases. Our targeted ammonia capacity is 500 g, which will supply roughly 1500 W-h of electrical energy from a fuel cell. The ammonia-storage system should have a total volume of about 1 to 2 liters and preferably less. It is not feasible to decrease the volume to less than about 0.85 liters as this is the volume of 500 g of liquid ammonia.

**Compatibility with ammonia-based hydrogen generators:** The ammonia storage system must interface with ammonia-based hydrogen generators. These generators require the ammonia be delivered under a small positive pressure to force the ammonia through the reactor and the fuel cell. Contaminants should not be introduced into the ammonia as these might interfere with the operation of the reactor and/or fuel cell.

**Low cost per use:** Fuel-cell power systems must not be significantly more expensive than the military Primary Battery packs, which cost approximately \$1 per W-h. Preferably, the fuel-cell-based systems will be significantly less expensive on a per-use basis in addition to being significantly smaller and lighter than the Primary Battery/15 pouch.

**Safety:** The ammonia-storage system should be intrinsically safe. Military applications for these power systems will involve rough handling in rugged environments where it is possible (perhaps likely) that a thin-walled storage tank could be punctured. Certainly the possibility of puncture by bullets and shrapnel must not be overlooked as the resulting ammonia plume might pose a great danger to soldiers.

### 3.3 Release of Ammonia from Storage Vessels

Ammonia is a widely used industrial and agricultural chemical. Despite its toxicity, serious accidents are rare because safety procedures and regulations have been developed to guard against accidental releases. These regulations were drafted principally for relatively large storage vessels and railcars, so their application to compact

<sup>1</sup> This value refers only to the fuel-storage components. The mass of the fuel cell and microreactor system are not included.



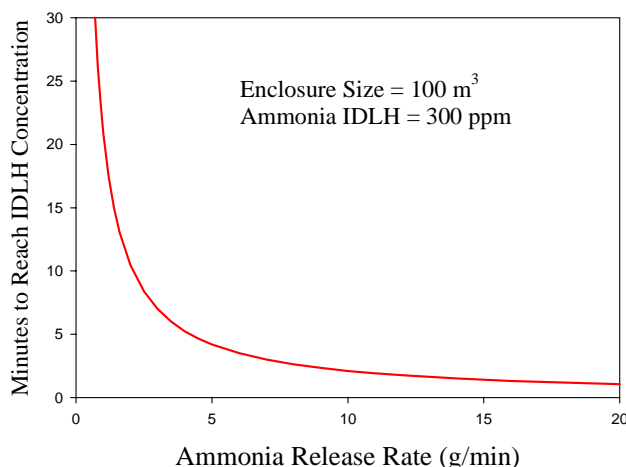
hydrogen generators is not entirely appropriate. Further, the ammonia-based power supplies are intended for use in a wide variety of environments – most of which are not considered (or are specifically outlawed) by existing procedures and regulations. Consequently, intrinsically safe storage of small amounts of ammonia is a relatively new challenge and there is little guidance from the chemical industry or lawmakers on how to approach the problem.

The vapor pressure of ammonia at room temperature is roughly 130 psia. Therefore, in the absence of any special storage media or adsorbents, ammonia must be stored in a pressure vessel. In the event the pressure vessel ruptures or is otherwise opened to the atmosphere, roughly 10% of the ammonia in the tank will quickly flash to vapor as the remaining liquid ammonia is cooled to near its atmospheric-pressure boiling point of  $-33^{\circ}\text{C}$ . For this reason, most large-capacity ammonia-storage tanks are refrigerated to near  $-33^{\circ}\text{C}$  to eliminate the possibility of a large ammonia release in the event the tank vapor space is inadvertently opened to ambient.

Potentially more dangerous, however, is the scenario wherein an ambient-temperature storage tank ruptures or is punctured below the liquid level. In this case, the 130 psia vapor above the liquid will forcibly expel the liquid out of the tank where much of the ammonia will volatilize upon contact with the surroundings. In this scenario, the entire tank contents might be expelled in a matter of seconds, thereby creating a dangerous atmosphere for nearby personnel. Clearly, the release of *liquid* ammonia directly to ambient in the event of tank failure must be avoided for the safe-storage system under consideration here.

The maximum allowable ammonia release rate for an ammonia-storage system designed for portable-power applications can be estimated based on an assumed enclosure volume and an allowable concentration of up to 300 ppm.<sup>2</sup> The time required to reach 300 ppm (IDLH) average ammonia concentration in a moderate-sized enclosure of  $100\text{ m}^3$  is plotted in Fig. 5 as a function of ammonia release rate. In smaller enclosures, the time to reach 300 ppm will be proportionally shorter. Based on Fig. 5, it is clear the maximum allowable release rate from a safe ammonia storage system should be on the order of 5 g/min or less. For safety in smaller enclosures, say  $10\text{ m}^3$ , the maximum release rate should be 0.5 g/min or less.

For our safe ammonia storage system, we are targeting a maximum ammonia release rate of approximately 1 g/min. This is roughly a factor of 4 greater than the ammonia



**Fig. 5.** Minutes to reach IDLH vs.  $\text{NH}_3$  release rate

release rate required to supply the 50-watt ammonia-decomposition reactor.

### 3.4 Safe Storage in Semi-Permeable, Lightweight Monoliths

With support from the U.S. Army Research Office via an SBIR contract, we developed a new approach for the safe storage of liquefied gases such as ammonia, propane, and butane.

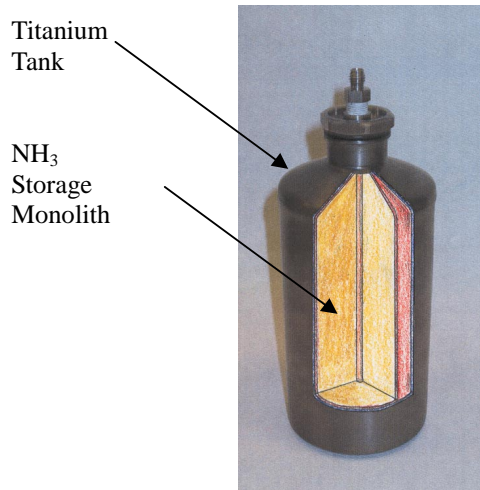
The safety concerns associated with storing liquid ammonia in thin-walled storage tanks led us to consider the use of semi-permeable, high-void-fraction monoliths as a safe storage media for liquid ammonia. Because the ammonia is stored as a liquid in high-void-fraction material, the storage density is high. But because the liquid ammonia is trapped within the pores of the monolith, a tank leak will not result in expulsion of liquid ammonia regardless of the leak location. The gas-phase ammonia can only escape at a slow rate, which is determined by the chemical and physical properties of the storage monolith.

The liquid ammonia is stored inside a low-permeability, high-void-fraction, monolithic structure that adds minimal weight yet effectively prevents rapid release of ammonia. A rigid tank, composed of metal, fiberglass, or a suitable plastic, surrounds the ammonia-storage monolith. Ammonia is forced into the monolith thereby filling the void spaces with liquid.

This approach offers very high storage density, compact size, and a controlled ammonia release rate even in the event of tank puncture. Rapid release of ammonia from the monolith is controlled by thermal and mass-transfer effects. To escape the monolith, the ammonia must permeate through the small pores to near the surface of the monolith.

<sup>2</sup> The Immediately Dangerous to Life and Health (IDLH) concentration for anhydrous ammonia is 300 ppm.

Fig. 6 shows a system concept sketch in which a piece of safe-storage material is sealed inside a thin-walled titanium tank. The lightweight titanium tank provides over 1000 psig of pressure resistance, and the monolith prevents rapid release ammonia in the event of tank puncture.



**Fig. 6.** Safe ammonia storage concept

The semi-permeable, high-void-fraction materials we are using for our safe-storage systems have a bulk density of 200 to 250 kg/m<sup>3</sup> and void fractions in excess of 80%. The composition and morphology of these materials are proprietary.

With a bulk density of 200 kg/m<sup>3</sup> and a void fraction of 85%, the storage monolith can achieve up to 72%wt. ammonia-storage density, which is close to the 75%wt. target value. If the monolith is positioned inside a metal tank, the tank mass will reduce this storage density to about 60%wt. However, the monolith is rigid and can support considerable compressive and tensile stress, so if the surface of the monolith can be sealed with a thin layer of plastic or metal foil then the overall storage density can be increased to 70%wt.

### 3.5 NH<sub>3</sub> Release Modeling and Performance

Release of gas from the storage monoliths is accurately described by a simple mathematical model in which transport of the gas through the monolith is characterized by an effective diffusion coefficient. The driving force for gas release is the pressure gradient between the liquefied gas inside the monolith and the ambient surroundings.

A numerical model was developed in an effort to allow prediction of ammonia release rates from different sizes and shapes of storage monoliths. Gas release from the monoliths was approximated by diffusion of a component out of a homogeneous volume. The governing equation for this process is:

$$\frac{\partial \rho_A}{\partial t} = D_{eff} \left( \frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2} \right) \quad (2)$$

where  $\rho_A$  is the local density of ammonia,  $t$  is time,  $D_{eff}$  is the effective diffusivity of ammonia through the storage monolith, and  $x$ ,  $y$ , and  $z$  are dimensions in rectangular coordinates. This equation was solved numerically for storage monoliths of various sizes and shapes.

The numerical model results indicate the targeted 1 g/min ammonia release rates from a 1-liter monolith are readily achieved when the effective diffusivity for ammonia release is on the order of 10<sup>-9</sup> m<sup>2</sup>/s. Our storage-monolith development efforts are focused on materials with approximately this  $D_{eff}$  value.

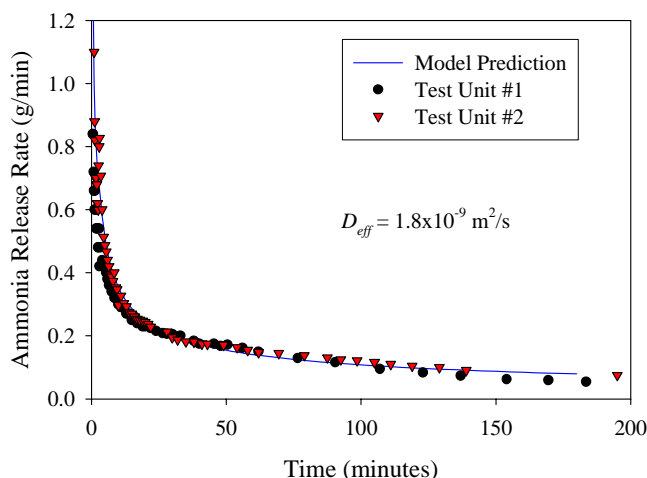
One storage material formulation has a bulk density of 200 kg/m<sup>3</sup> and a void fraction in excess of 80%. The measured  $D_{eff}$  for ammonia release from this material is 1.8x10<sup>-9</sup> m<sup>2</sup>/s. A cylindrical piece was installed in a lightweight, plastic tank to create the safe-ammonia-storage prototype shown in Fig. 7.



**Fig. 7.** Safe NH<sub>3</sub> storage prototype tank

The Fig. 7 storage monolith was filled with ammonia and then tested by opening the tank valve and allowing ammonia to vent to ambient while monitoring the tank mass. The ammonia-release-rate data are shown in Fig. 8. During the first minute, the release rate briefly exceeds 1 g/min as ammonia near the monolith surface is released, but thereafter the release rate is below the 1 g/min target. The solid line in the plot reflects model predictions for  $D_{eff} = 1.8 \times 10^{-9}$  m<sup>2</sup>/s, which was measured independently using the observed release from a 3-cm cube of monolith with the same composition.

The gas release rate can be adjusted either by altering the storage-media properties, and thereby changing the value of  $D_{eff}$ , or by simply changing the monolith geometry. Monoliths with a high surface-area-to-volume ratio will release gas more quickly than those with a lower ratio. We demonstrated this effect by covering a fraction of the monolith surface with a suitable epoxy. The ammonia release rate was reduced by roughly a factor of four, which was consistent with predictions of the numerical model.



**Fig. 8.** Ammonia release from prototype

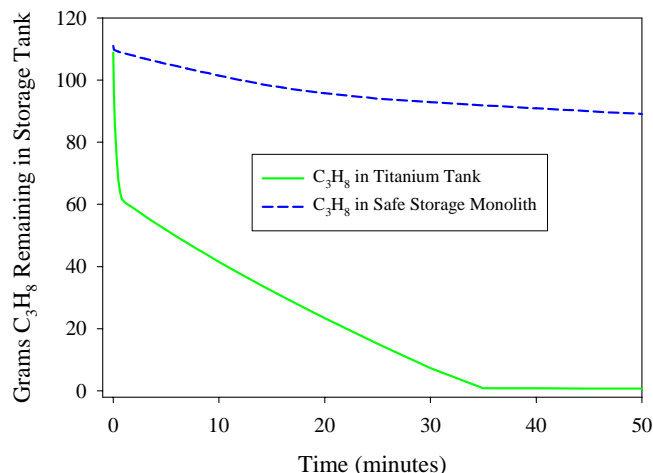
We are now able to adjust the ammonia release rate characteristics of the safe-storage prototypes over the range of interest for compact power systems (roughly 0.1 to 10 g/min) by adjusting the shape of the monolith and the fraction of monolith surface available for gas release.

In addition to our ammonia-release tests, we have conducted similar tests with butane and propane. These liquefied hydrocarbon gases can be used in compact power systems under development elsewhere (e.g., Chellappa et al., 2004) as well as in a wide variety of consumer products unrelated to compact power.

Fig. 9 compares the release of propane from a titanium fuel tank (Fig. 4a) to that from a lightweight tank made using our safe-storage monolith. At time=0, the valve on the top of each tank was opened. Nearly half the propane in the titanium tank exits through the valve in the first minute of the test. This contrasts sharply with the slow, steady release of propane from the safe-storage tank. During the first minute of the test, the rate of propane release from the safe-storage tank is about 100 times slower than that from the titanium tank. Similar results are obtained for tests using butane and ammonia.

Currently, we are working on lightweight methods to seal the external surface of the storage monolith. A variety of polymeric materials and metals are suitable for use with butane and propane, but ammonia is an effective plasticizer for many polymers and is also corrosive to many metals. Achieving a robust, lightweight seal on the external surface of the monolith is the key to maintaining the high energy density of fuel stored in the safe-storage monolith.

Fig. 10 shows a cylinder of safe-storage monolith inside a Kevlar/epoxy fiber-wound tank. The tank has a mass of 170 g, with 70 g being storage monolith. The tank diameter is 5.3 cm and its length is 21 cm. The ammonia capacity is 180 g, so the effective storage density is 50% wt. With



**Fig. 9.** Propane release from titanium tank and safe-storage monolith



**Fig. 10.** Kevlar/epoxy tank surrounding monolith

larger monolith sizes, the storage density increases because tank mass varies with monolith surface area but ammonia-storage capacity is proportional to monolith volume.

### 3.6 Tank Puncture Testing

The gas release tests described in Section 3.5 simulate failure of the tank valve or a downstream component such as tubing connecting the tank to the ammonia-decomposition reactor. In this case, the monolith releases gas via the pathway expected during normal operation. A more challenging scenario is direct puncture of the tank wall by a sharp object or bullet. In this case, gas release proceeds via the newly created hole or tear in the external tank.

We performed a series of tests to compare release of gas from our safe-storage monolith to that from conventional thin-walled tanks. For reasons of personnel safety, propane was used for these tests rather than ammonia. A 0.22-caliber rifle was used to puncture two storage tanks containing propane: (1) a 0.6-L titanium tank; and (2) a safe-storage monolith with its external surface sealed using a



suitable thermoset plastic. Each tank contained approximately 160 g of fuel before the tests.

Fig. 11 shows photographs of the tanks roughly 100 ms after bullet impact. The entire contents of the titanium tank were released in approximately 1 second. A mixture of vapor and liquid fuel was forcibly expelled from the holes created by the bullet impact. In the case of the safe-storage monolith, however, only 5 to 10 grams of propane was released in the first several seconds after impact – an amount roughly corresponding to the volume of the hole created by the bullet. The remaining 150+ grams of propane in the monolith was slowly released through the bullet hole over the next several hours.



(a)



(b)

**Fig. 11.** Propane release from (a) titanium tank and (b) safe-storage monolith

## CONCLUSIONS

MesoSystems Technology, Inc. and Intelligent Energy, Inc. have developed a compact, lightweight system that produces hydrogen from ammonia by thermocatalytic decomposition. The microreactor-based hydrogen generator produces power with an energy density of approximately 500 W-h/kg for a 1250 W-h capacity. In addition, we developed and a safe method for storing

flammable and toxic fuels in lightweight containers. This new fuel-storage technology is applicable to a variety of compact-power systems and may offer new commercial applications that have previously been unrealized due to concerns over rapid release of toxic and flammable gases.

Deployment of safe, compact hydrogen sources benefits the U.S. Army by reducing the weight and cost associated with battery-based power supplies. This improves both the sustainability and the responsiveness of U.S. Army fighting forces.

## ACKNOWLEDGEMENTS

This work is funded by the U.S. Army Research Office under Phase II Small Business Innovation Research contract DAAD19-03-C-0134.

## REFERENCES

- Appleby, A.J., and F.R. Foulkes. 1989. *Fuel Cell Handbook*. Van Nostrand Reinhold, New York.
- Blomen, L., and M.N. Mugerwa. 1993. *Fuel Cell Systems*. Plenum Press, New York.
- Bloomfield, D.P., V.J. Bloomfield, P.D. Grosjean, and J.W. Kelland. 1995. *Mobile Electric Power*. Analytic Power Corp., NTIS Report ADA296709.
- AS Chellappa, TR Vencill, and MR Powell. 2004. "Advances in Pure Hydrogen Production for Fuel Cells using Membrane Steam Reformers." AICHE Spring 2004 Meeting, April 26-29, 2004. New Orleans, Louisiana.
- Nielsen, A., 1995: *Ammonia: Catalysis and Manufacture*. Springer-Verlag, New York.
- Powell, MR, MS Fountain, CJ Call, AS Chellappa. 2002. "Ammonia-Based Hydrogen Generation for Fuel Cell Power Supplies." Army Science Conference 2002, Orlando, Florida. Dec. 2-5, 2002.
- Powell, MR, M. Fountain, and CJ Call. 2001. "Ammonia-Based Hydrogen Generator for Portable Fuel Cells." *Proceedings International Conference on Microreaction Technologies (IMRET 5)*. 2001.
- Schmidt, J., F. Lynch, J. Wilkes, R. Lucero, and R. Vaughn, 2002: "Ammonia-Hydride Storage Materials and Hydrogen Generators." Electrochemical Society 201st Meeting, May 12-17, 2002, Philadelphia, Pennsylvania.
- T-Raissi, A., 2002: "Technoeconomic Analysis of Area II Hydrogen Production – Part II: Hydrogen from Ammonia and Ammonia-Borane Complex for Fuel Cell Applications." *Proceedings of the 2002 U.S. DOE Hydrogen Program Review*. NREL/CP-610-32405.
- Twigg, M.V., 1997: *Catalyst Handbook*. Manson Publishing, London.